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BROWN UNIVERSITY *Providence, Rhode Island • 02912*

DIVISION OF ENGINEERING

Sept 30 1992

To: Dr. Alvin Goodman, Electronics Division, Office of Naval Research

cc: Administrative Grants Officer, ONR
Director, Naval Research Laboratory
Defense Technical Information Center

From: D.C. Paine, Assistant Professor of Engineering and Principal Investigator

Re: End-of-Fiscal-Year Summary

Contract Title: The Properties of Thermally Passivated $Si_{1-x}Ge_x$ Produced Using High Pressure Techniques (and related augmentation awards)
Contract Number: N00014-91-J-1837
R&T Numbers: 4145308---01,02,03

This review covers the three combined efforts described in the original proposals as:

4145308-01: "The Properties of Thermally Passivated $Si_{1-x}Ge_x$ Produced Using High Pressure Techniques" (original proposal) 01 Jul 1991 through 30 Jun 1992.

4145308-02: "Thermally Passivated $Si_{1-x}Ge_x$ Produced Using High Pressure Techniques (Expansion to original Proposal)": 01 Jul 1991 through 31 May 1995

4145308-03: " Synthesis and Characterization of Thin Film Electronic Oxides Using Ultra High Pressure Oxidation": (AASERT Award) 01 Jul 1991 through 31 May 1995

A. Summary of Research Goals

Since the July 1 1991 start date of this work, research has been pursued on the use of ultra high pressure oxidation for the growth of electronic quality MOS oxides on $Si_{1-x}Ge_x$. High pressure, low temperature oxidation allows the formation of compositionally congruent oxides from $Si_{1-x}Ge_x$ and eliminates the interfacial enrichment of Ge that is seen during conventional oxidation processes. Specific studies of the congruent $Si_{1-x}Ge_xO_2$ grown from $Si_{1-x}Ge_x$ that were carried out over the past year include: (i) oxidation kinetic studies, (ii) optical characterization (Raman and FTIR), (iii) MOS C-V measurements, and (iv) high resolution TEM. During this work a second important research direction was initiated, consistent with the AASERT task (4145308-03), in which high pressure oxides of $Si_{1-x}Ge_xO_2$ were used for the synthesis of nanocrystalline Ge.

B. Significant Results

During the past year we have established kinetic data (thickness, time at temperature; 500 and 550 °C) for the growth of congruent oxides of $Si_{1-x}Ge_xO_2$ using pure O_2 at 2500 to 10,000 psi and with controlled quantities of moisture in the range from ≈10 ppm to direct hydrothermal oxidation using water above its critical point. The oxidation rate was enhanced by low levels (≈10 ppm) of H_2O which has an increasing effect with increasing pressures in determining the kinetics of oxidation of $Si_{1-x}Ge_x$ over the compositional range 5 to 40 at% Ge.

Interface characterization of high pressure oxides of $Si_{1-x}Ge_x$ was accomplished using Raman and lattice resolution TEM to establish the chemical and atomic properties of these congruent oxides. Raman revealed that Ge was not accumulated at the the oxide/alloy interface while TEM studies revealed a nearly atomic flat interface comparable to conventionally grown Si/SiO_2. These results suggest that the as-grown oxides have an physical interface structure that is consistent with MOS device application

Electronic measurements have proceeded using, primarily, high frequency C-V analysis and the Terman method for establishing interface trap density by comparison of the ideal and measured C-V curves. We can demonstrate mid-gap interface trap densities of $1x10^{12}/cm^2eV$. Continuing efforts are being made to better establish the interface quality — and the source of the relatively high value of D_{it} — using quasi-static C-V analysis which has recently become available in our laboratory.

The chemical stability of as-grown $Si_{1-x}Ge_x$-oxides have been evaluated through high temperature annealing studies using an RTA and vacuum, N_2, and N_2/H_2 gas environments. We have established that the TEM images and the FTIR and XPS spectra remain unchanged after annealing for up to 1 hour at 700 °C. Above 800°C the GeO_2 component of the oxide becomes reduced through either Si or H_2 diffusion into the oxide (depending on the anneal atmosphere) which results in the precipitation of Ge. We have been able to control the precipitation reaction to produce a uniform dispersion of nanocrystalline (1-5 nm) Ge in an SiO_2 matrix. This result is a particularly interesting additional research direction since nanocrystalline Ge may display quantum confinement behavior and, according to recent literature reports, visible photoluminescence.

C. Plans for Next Year

(i) We intend to incorporate a moisture meter into our HPO system in order to unambiguously establish the moisture content of the oxygen before and after each oxidation run. In addition we will modify the HPO system to allow controlled quantities of water to be introduced into the reactor. This will provide for greatly improved process control and oxide growth repeatability for the formation of MOS oxides from alloys of $Si_{1-x}Ge_x$.

(ii) Through this grant we have purchased a HP4061A semiconductor analysis system which has been set-up for quasistatic and high frequency C-V analysis. It will also be used to study oxide breakdown and leakage. In addition to providing detailed electronic analysis of the oxide/alloy interface, it will also be used for studying the quality of the oxides grown under various conditions in an effort to optimize the $Si_{1-x}Ge_x$-oxides for MOS applications.

(iii) Over the past year we have discovered an entirely novel method for the synthesis of nanocrystalline Ge precipitates that are defect-free, uniform in size, and are well dispersed in a passivating SiO_2 matrix. This method uses high pressure oxidation of $Si_{1-x}Ge_x$ alloys to form compositionally congruent oxides of $Si_{1-x}Ge_xO_2$ from which precipitates of nanometer-sized Ge particles form when the oxide is annealed above 800°C. We intend to use this method to grow structures which consist of monodisperse Ge precipitates of size ranging from 1 to 50 nm for use in photoluminescence studies.

OFFICE OF NAVAL RESEARCH
PUBLICATION/PATENTS/PRESENTATION/HONORS REPORT
for
1 Oct 91 through 30 Sept 92

R&T Number: 4145308-01, 02, 03

Contract/Grant Number: N00014-91-J-1837

Contract/Grant Title: The Properties of Thermally Passivated $Si_{1-x}Ge_x$ Produced using High Pressure Techniques

Principal Investigator:

Mailing Address:

Phone Number (with Area Code):

E-Mail Address: David_Paine@Brown.edu

a. Number of Papers Submitted to Referred Journal but not yet published: 1

b. Number of Papers Published in Referred Journals: 1
(list attached)

c. Number of Books or Chapters Submitted but not yet Published: 0

d. Number of Books or Chapters Published: 0
(list attached)

e. Number of Printed Technical Report & Non-Referred Papers: 1
(list attached)

f. Number of Patents Filed: 0

g. Number of Patents Granted: 0
(list attached)

h. Number of Invited Presentations at Workshops or Prof. Society Meetings: 0

i. Number of Presentation at Workshop or Prof. Society Meetings: 2

j. Honors/Awards/Prizes for Contract/Grant Employees:
(list attached. this might Include Scientific Soc. Awards/Offices, Promotions, Faculty Award/Offices etc.) 2

k. Total number of Graduate Students and Post-Docs Supported at least 25%, this year on this contract,grant:
Grad Students 1 and Post Docs 0

How many of each are females or minorities? (These 6 numbers are for ONR's EEO/Minority Reports; minorities Include Blacks, Aleuts Amindians, etc and those of Hispanic or Asian extraction/nationality. This Asians are singled out to facilitate meeting the varying report semantics re "under-represented")

- Grad Student Female 1
- Grad Student Minority 1
- Grad Student Asian e/n 1
- Post-Doc Female 0
- Post-Doc Minority 0
- Post-Doc Asian e/n 0

GRANT NUMBER: N00014-91-J-1837/P00001

FORM A2-2

AUGMENTATION AWARDS FOR SCIENCE & ENGINEERING RESEARCH TRAINING (AASERT) REPORTING FORM

The Department of Defense (DOD) requires certain information to evaluate the effectiveness of the AASERT program. By accepting this Grant Modification, which bestows the AASERT funds, the Grantee agrees to provide the information requested below to the Government's technical point of contact by each annual anniversary of the AASERT award date.

1. Grantee identification data: (R & T and Grant numbers found on Page 1 of Grant)

a. Brown University
University Name

b. N00014-91-J-1837
Grant Number

c. 4145308---01, 02, 03
R & T Number

d. David C. Paine
P.I. Name

e. From: 04 Apr '92 To: 30 Sept. '92
AASERT Reporting Period

NOTE: Grant to which AASERT award is attached is referred to hereafter as "Parent Agreement."

2. Total funding of the Parent Agreement and the number of full-time equivalent graduate students (FTEGS) supported by the Parent Agreement during the 12-month period prior to the AASERT award date.

a. Funding: $ 28,334.00

b. Number FTEGS: 0

3. Total funding of the Parent Agreement and the number of FTEGS supported by the Parent Agreement during the current 12-month reporting period.

a. Funding: $ 35,000.00

b. Number FTEGS: 0

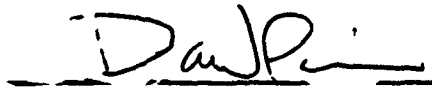
4. Total AASERT funding and the number of FTEGS and undergraduate students (UGS) supported by AASERT funds during the current 12-month reporting period.

a. Funding: $ 33,428.00 (Since 04 April '92)

b. Number FTEGS: 1

c. Number UGS: 2

VERIFICATION STATEMENT: I hereby verify that all students supported by the AASERT award are U.S. citizens.



Principal Investigator

30 September 1992
Date

E. List of Publications/Reports/Patents/Graduates

(i) a Papers published in refereed Journals and Proceedings (including those accepted for publication)

D.C. Paine, C. Caragianis, and Y. Shigesato, "Hydrothermal Oxidation of Alloys of $Si_{1-x}Ge_x$ for the Synthesis of Nanocrystalline Germanium", *Appl. Phys. Letts,* 60(23), pp. 2886-2888(1992).

C. Caragianis, A.F. Schwartzman, and D.C. Paine, "Oxidation of $Si_{1-x}Ge_x$ at Elevated Pressure", Vol 251, Materials Research Society Symposium S: Pressure Effects on Materials Processing and Design, 1991 Fall Meeting

(i) b Papers Submitted but not yet published:

C. Caragianis, Y. Shigesato, and D.C. Paine, "High Pressure Oxidation of Alloys of $Si_{1-x}Ge_x$ for MOS Applications", *J. ECS, submitted July 1992*

Y. Shigesato and D.C. Paine, "A Study of the effect of Sn doping on the electronic transport properties of thin film indium tin oxide", *Appl. Phys.Lett., Submitted Sept 1992*

(ii) Technical Reports and non-refereed papers

C. Caragianis, Y. Shigesato, and D.C. Paine, "High Pressure Oxidation For Low Temperature Passivation of $Si_{1-x}Ge_x$ Alloys", to be published in the proceedings of the Second Symposium on the Physics and Chemistry of SiO_2 and the Si/SiO_2 Interface, edited by Bruce Deal and C.R. Helms, Plenum Publishing.

(iii) Invited Presentations

Stevens Institute of Technology, Department of Materials Science and Engineering, Oct. 23 1991, "Effect of Strain on the Kinetics of Solid Phase Epitaxical Growth"

University of Rhode Island, Center for Thin Film and Interface Research, April 24 1992, "Electron Microscopy for Interface Investigation".

(iv) Contributed Presentations

D.C. Paine, 181 st ECS Meeting, The Second Symposium on the Physics and Chemistry of SiO_2 and the Si/SiO_2 Interface, St. Louis, May 17-22, 1992.

F. Honors and Awards

Member of the Electronic, Magnetic and Photonic Materials Steering Committee of the TMS, 1991/92.

Guest Editor of the Feb. '93 issue of JOM special topics section: Interface stability and lower dimensional structures.

G. Other Sponsored Research (P.I.)

National Science Foundation, Brown University Materials Research Group, "Micromechanics of failure resistant materials", (jointly with ten colleagues at Brown University).

National Science Foundation, $30,000.00, Engineering Research Equipment, Ultra High Pressure Oxidation Reactor and Compressor.

National Science Foundation,
$55,0000.00/yr for 3 yrs, "Novel materials synthesis by HPO".